Biogenic Emissions

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Introduction

- Biogenic hydrocarbons, including isoprene and monoterpenes, are emitted from a wide range of natural, agricultural, and ornamental vegetation.
- The National Research Council (1991) noted that hydrocarbon emissions from vegetation are not well understood. However, experimental and modeling studies have shown that biogenic hydrocarbons can constitute a significant contribution to the overall VOC emission inventory in both urban and rural regions and, on average, biogenic hydrocarbons are two to three times more reactive than emissions from mobile sources (Winer et al., 1995).
- The need for accurate inventories of biogenic hydrocarbons becomes more important as their relative contributions increase with concurrent declines in anthropogenic hydrocarbons and NO_x emissions due to implementation of emissions control regulations.
- The only biogenic hydrocarbon on the PAMS target list is isoprene. Some PAMS sites also monitor for α- and β-pinenes.

Most Abundant VOCs Identified As Emitted From Plant Species

Species/Class	Example(s)	Half-Life (hr)[a]
Isoprene	Isoprene	1.8
Monoterpenes	limonene	1.1
	camphene	3.5
	α-pinene	3.4
	β-pinene	2.3
n-Alkanes	n-hexane	>48
	C_{10}-C_{17}	7-31
Alkenes	1-decene	4
Aromatics	p-Cymene	24
Sesquiterpenes	β-Caryophyllene	
Alcohols	cis-3-hexen-1-ol	
Aldehydes	n-hexanal	7.4
Ketones	2-heptanone	>24

[a] Half-life based on reaction with OH radical.

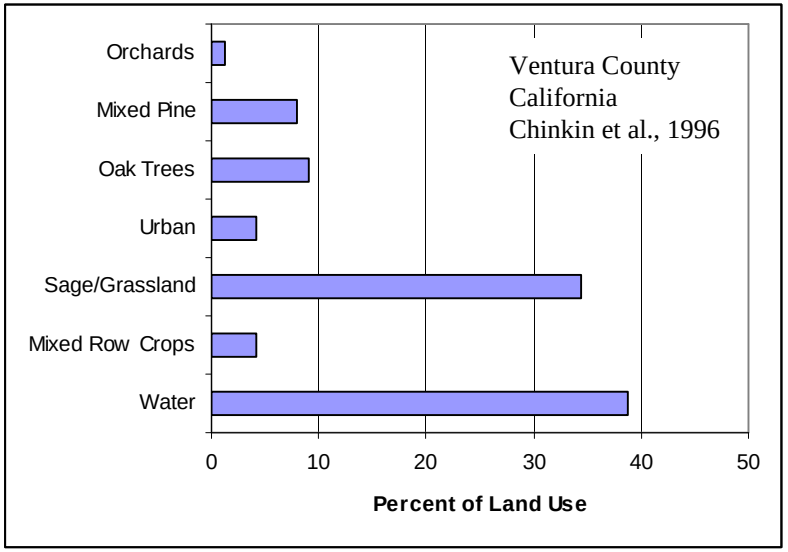
Sources:
Winer et al., 1992, 1989
Grosjean et al., 1996
Guenther et al., 1996
Carter 1991, 1994

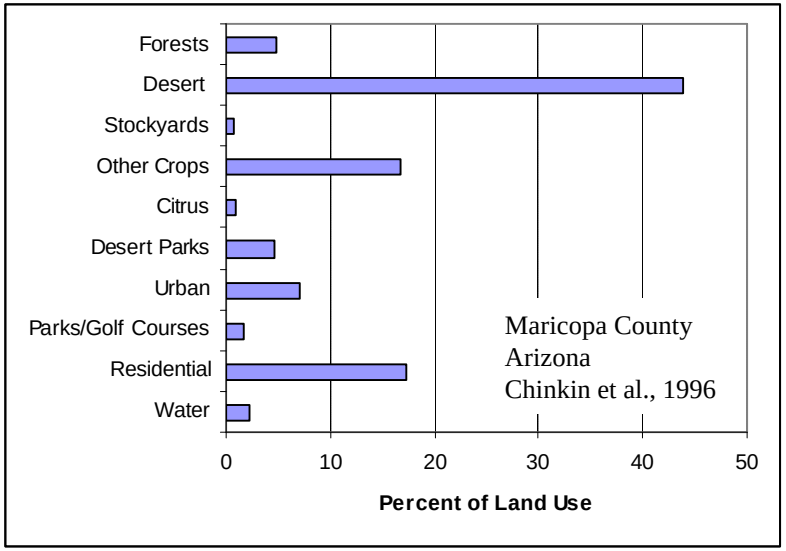
Characteristics of Isoprene Concentrations

- Isoprene emissions vary significantly due to environmental factors including sunlight intensity and air temperature. Estimation algorithms (such as the EPA Biogenic Emissions Inventory System - BEIS) show that isoprene emissions should be expected to peak about midday. Ambient data show isoprene peaks from midday to early evening.
- Because biogenic emissions vary by plant species as well as with environmental influences, biogenic spatial emission patterns are not expected to be homogeneous. Researchers have noted that biogenic emission densities can range over several orders of magnitude.
- Variations in the diurnal biogenic emission patterns in different portions of the study area are expected to be observable in the ambient data.
- Isoprene is an abundant biogenic hydrocarbon species and is often an important contributor to total mass at urban and rural monitoring locations.

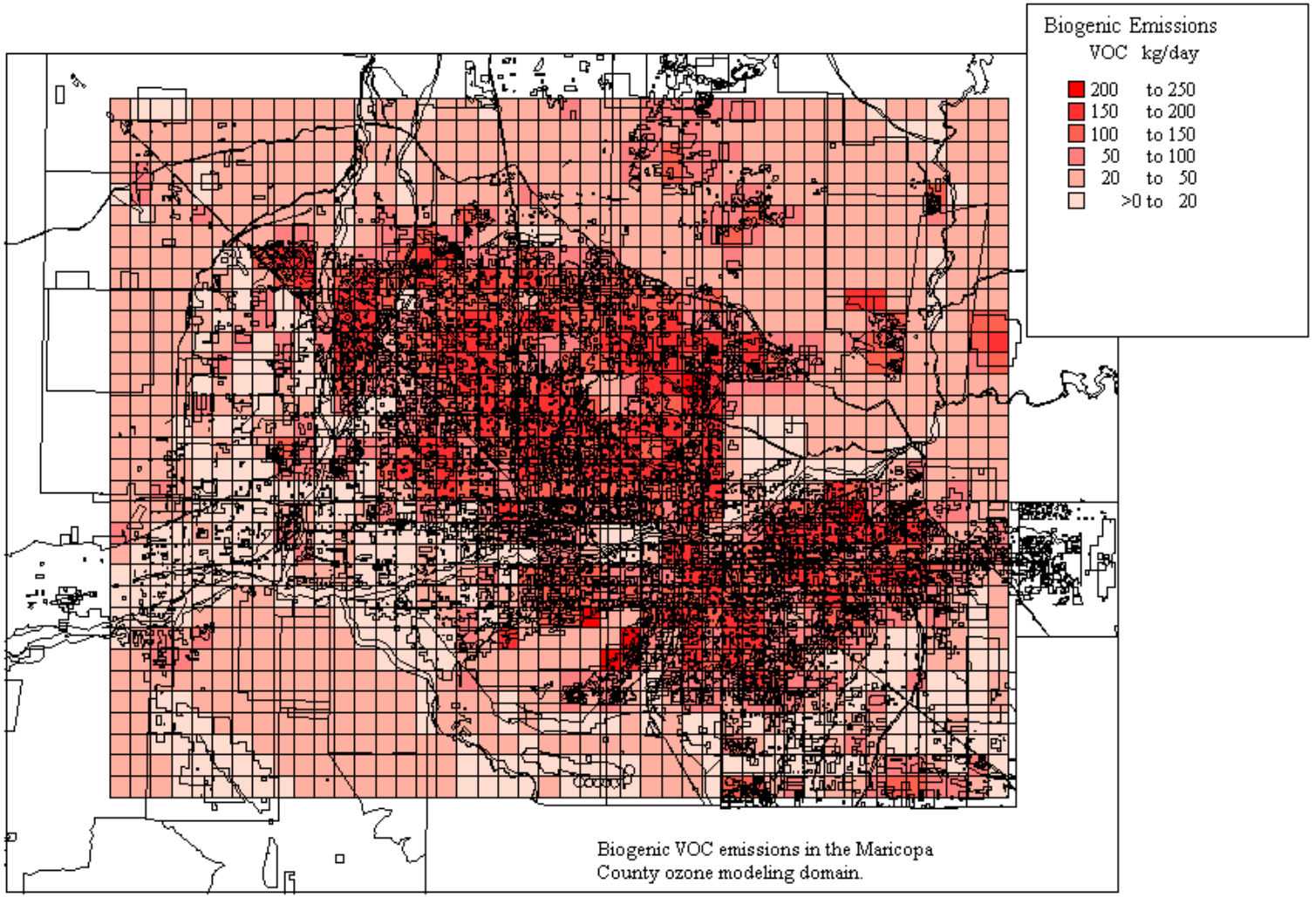
Example Land Use Coverage by Category

- It is important to inspect the land use coverage by category for an ozone modeling domain based on the most recent assessment of land use.
- These two examples show a coastal county in California with the modeling domain comprised of mostly ocean and sage/grassland and a southwestern county comprised mostly of desert. The biogenic emissions for these two counties are likely very different.





Biogenic VOC Emissions Density



Example biogenic VOC emissions density plot. This figure shows biogenic VOC emissions in the Maricopa County ozone modeling domain (Chinkin et al., 1996). Emissions were based on a modified version of BEIS-2.

The biogenic VOC emissions are highest for the urban areas in this domain.

Important Vegetation for Biogenic Emissions

Example vegetation/biogenic species by region:

Region	Biogenic Species	Predominant Vegetation*
Southwestern United States	Isoprene	Oak (mostly), citrus, eucalyptus
	Monoterpenes	Pine, citrus, eucalyptus
Northeastern United States	Isoprene	Oak, spruce
	Monoterpenes	Maple, hickory, pine, spruce, fir, cottonwood

* estimated using BEIS-2

For the two regions shown here, the next step in identifying important biogenic species is to determine land use/land coverage. Note that, in the Southeast (not listed in the above table), kudzu is an important source of isoprene and it may not be categorized as traditional sources of land use data. (Chinkin et al., 1996a,b; Chameides and Cowling, 1995)

Example Data Analyses (1 of 5)

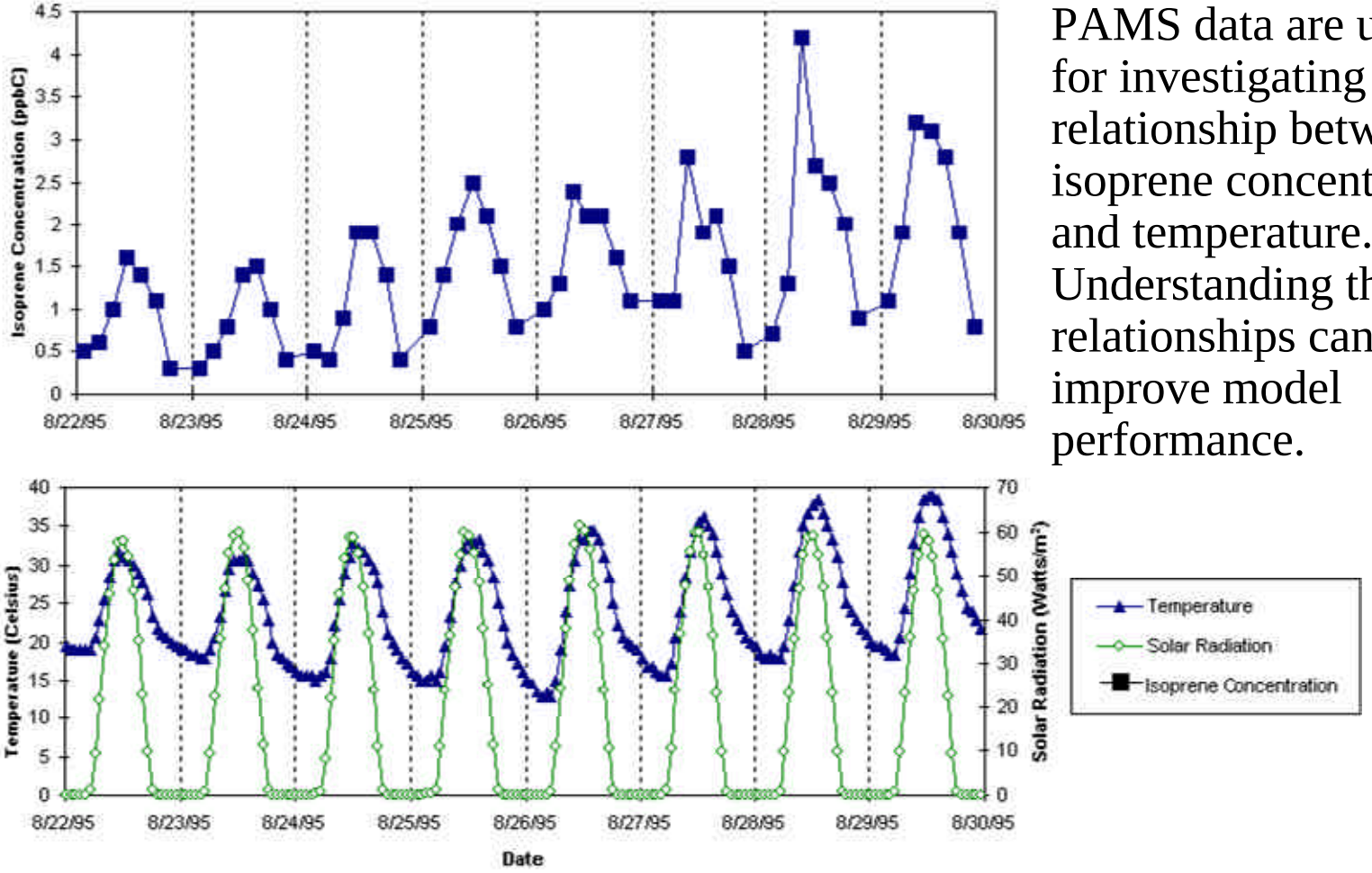
Temporal Characteristics of Biogenics

- Inspect diurnal profiles using box plots, line graphs of daily concentrations, and plots of hourly summary statistics.

Spatial Characteristics of Biogenics

- Prepare spatial plots of peak concentrations or of concentrations at a given hour.
- Compare peak concentrations and diurnal behavior to other areas and to other measurements (i.e., temperature, solar radiation).
- Quantify concentration and weight fraction of isoprene as a function of time of day.

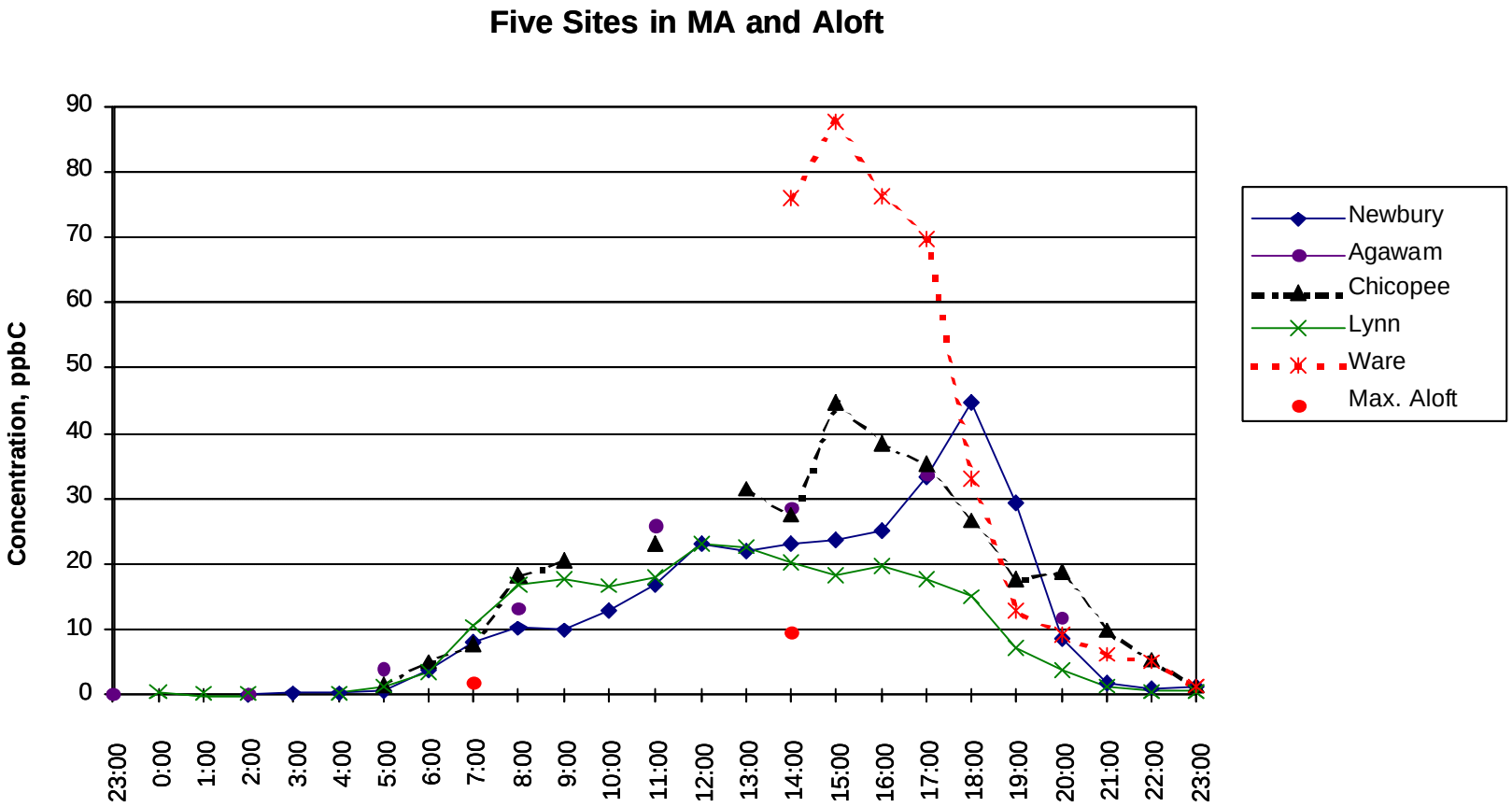
Example Data Analyses (2 of 5)



PAMS data are useful for investigating the relationship between isoprene concentrations and temperature. Understanding these relationships can help improve model performance.

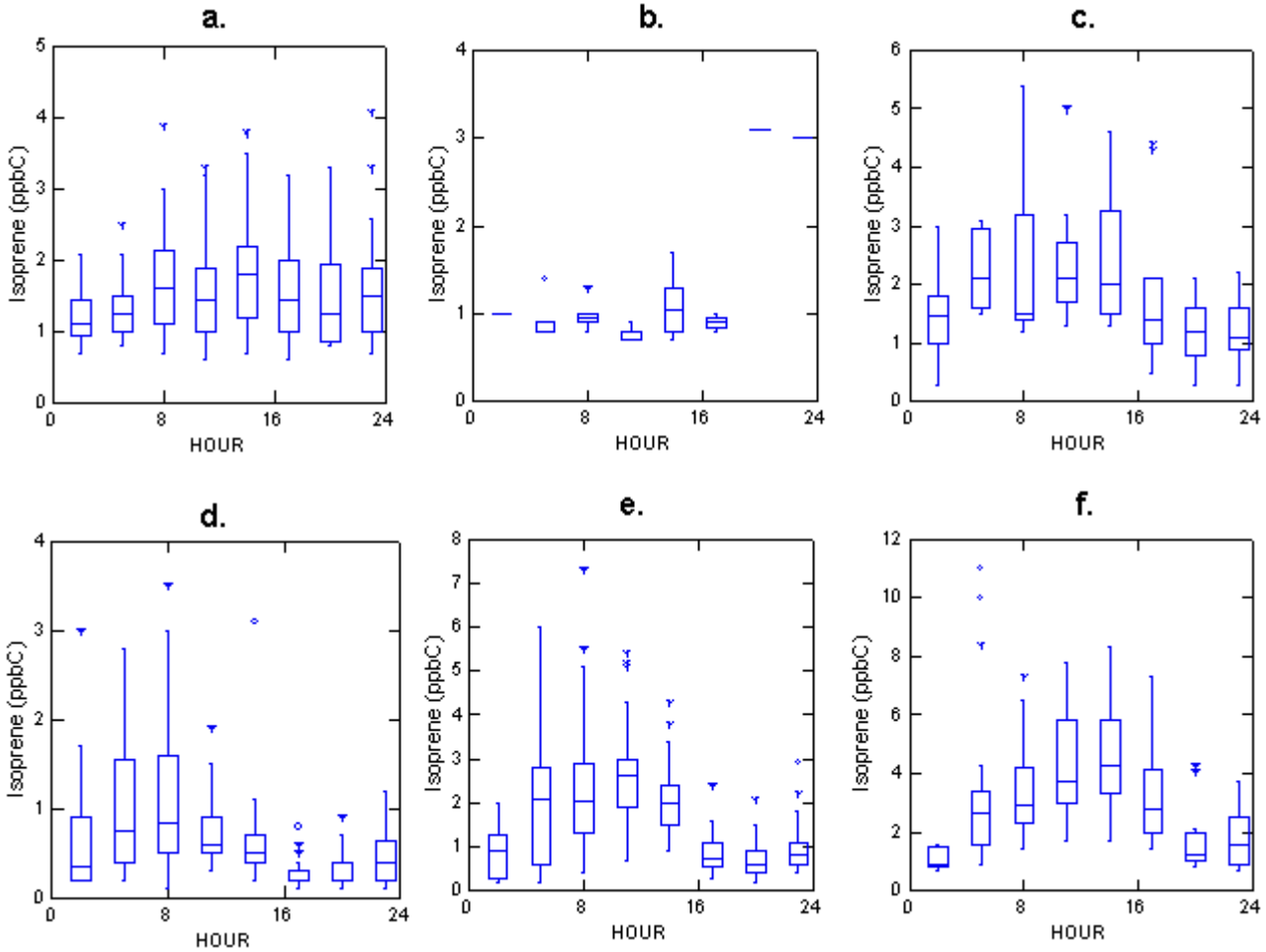
Three-hour average isoprene concentrations and hourly temperature and solar radiation data collected at Pico Rivera, CA during August 22-29, 1995. The peak daily temperature and isoprene concentrations rose between August 24 and 26.

Example Data Analyses (3 of 5)



Isoprene concentrations at five sites in Massachusetts and the maximum isoprene concentrations measured by aircraft on July 14, 1995 (in EST). This plot illustrates the following: 1) Peak daily isoprene concentrations can vary over a wide range of concentrations (e.g., 20 to nearly 90 ppbC); 2) the time of the peak isoprene concentrations can vary among sites (1200 EST to 1800 EST in this example); and 3) the distribution of isoprene concentrations throughout a modeling domain (vertically as well as horizontally) can vary widely.

Example Data Analyses (4 of 5)



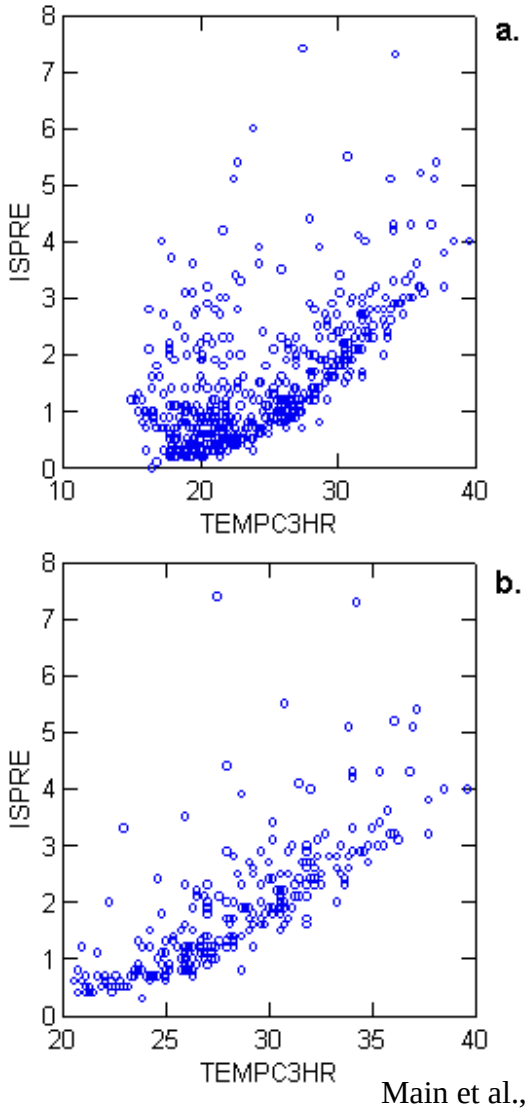
Main et al., 1999

Box-whisker plots of isoprene concentrations in 1997 at Southern California PAMS sites a) Azusa, b) Banning, c) Burbank, d) Hawthorne, e) Pico Rivera, and f) Upland. Isoprene concentrations were relatively low at all the sites compared to Northeastern PAMS sites. Concentrations were highest at Upland. The diurnal profile at Upland is characteristic of isoprene.

Example Data Analyses (5 of 5)

- It is important to explore the relationship between isoprene concentrations and other measurements. In this example, scatter plots of isoprene concentration (ISPRE) in ppbC versus temperature in °C (TEMP3HR) are shown.
- The top plot compares data from all sampling periods (r=0.61) and the bottom compares data during daytime sampling periods only (r=0.77).
- Poor to moderate correlations are observed with some improvement seen in the daytime only comparison. Understanding these relationships helps improve biogenic emissions modeling.

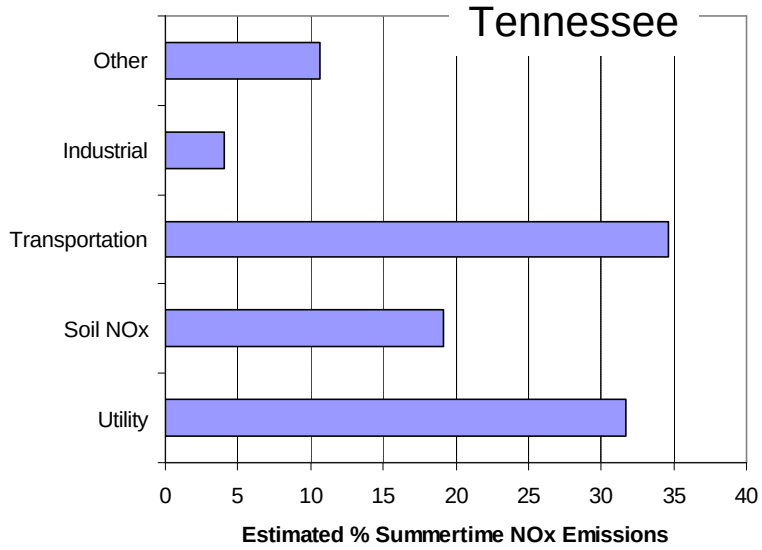
Pico Rivera, CA 1997



Main et al., 1999

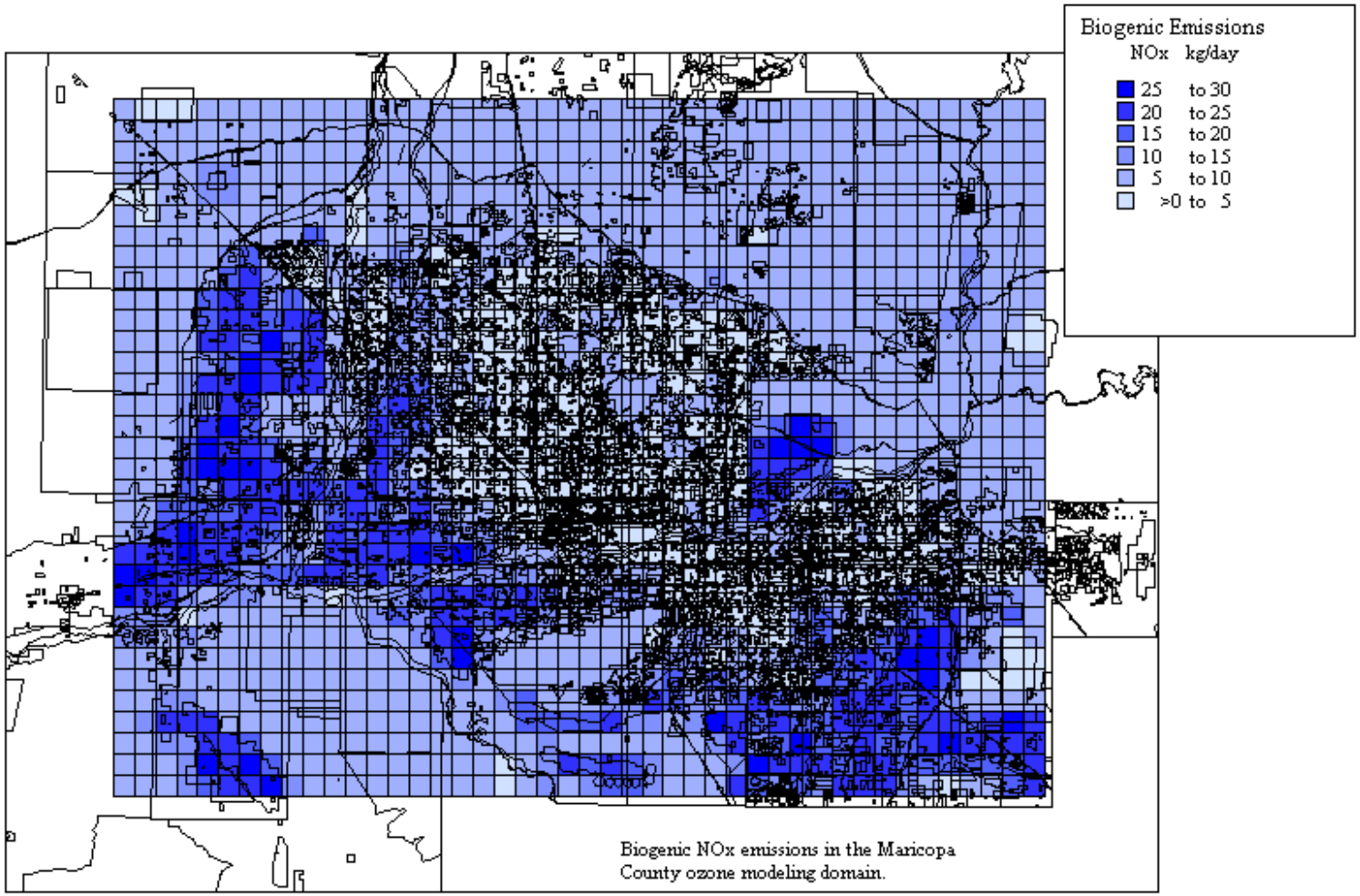
Biogenic Sources of NO_x

- In addition to "traditional" sources, nitrogen oxides are also emitted from soils.
- In the example provided, soil NO_x is estimated to be an important contributor to overall NO_x emissions.
- Research shows that soil NO_x emissions increase with temperature, are highest in soils with enhanced nitrate concentrations, and often are increased briefly after a light rainfall (Williams et al., 1991).



Soil NO_x based on TVA Giles County measurements. Other data from the 1985 NAPAP inventory. Adapted from Valente and Thornton, 1993.

Biogenic NO_x Emissions Density



Example biogenic NO_x emissions density plot. This figure shows biogenic NO_x emissions in the Maricopa County ozone modeling domain (Chinkin et al., 1996). Emissions are based on a modified version of BEIS-2.

Biogenic NO_x emissions are highest outside the urban areas, primarily in the agricultural areas.

Biogenic Emission Research Topics (1 of 2)

Research on the following types of biogenic emissions issues is currently in progress:

- Are isoprene concentrations measured at a PAMS site regionally, or are the concentrations only locally representative? How are concentrations at a monitor affected by a nearby vegetation canopy?
- Are other biogenic species important to the total VOC or to overall reactivity?
- Are unidentified biogenic species an important contributor to the unidentified hydrocarbon total?
- How do urban vs. rural biogenic concentrations differ, and what is the importance of these variations to formation of ozone at downwind sites?

Biogenic Emission Research Topics (2 of 2)

Research on the following types of biogenic emissions issues is currently in progress (concluded):

- What are the products of reaction from biogenic species (such as methylvinylketone – MVK)? Are these species readily measurable?
- What is the contribution to ambient NO_x levels from natural sources? How do natural source NO_x emissions compare to anthropogenic NO_x emissions?

Available Tools and Methods (1 of 2)

- Ambient data sources:
  - AIRS Data via public web: *http://www.epa.gov/airsdata*
  - AIRS AQS via registered users: register with EPA/NCC: (703) 487-4630
  - Maximum incremental reactivity factors: *http://www.cert.ucr.edu/~carter/reactdat.htm*
- Emissions and Land Use Data Sources:
  - Land use data available, for example, from the USGS at *http://edcwww.cr.usgs.gov/pub/data/LULC/*
  - Biogenic emissions using BEIS2.3. The Biogenic Emissions Inventory System allows users to estimate hourly emissions of biogenic VOC and soil NO_x emissions for any county in the contiguous United States. BEIS is available at *http://www.epa.gov/asmdnerl/biogen.html*

Available Tools and Methods (2 of 2)

- Emissions Processing Software:
  - SMOKE (*http://envpro.ncsc.org/products/smoke/*)
  - EMS95 (see *http://www.ladco.org*)
- Mapping and Gridding Software:
  - Surfer (*http://www.goldensoftware.com/*)
  - MapInfo (*http://www.mapinfo.com/*)
  - ArcInfo and ArcView (*http://www.esri.com/*)
  - SAS (*http://www.sas.com/*)
- Spatial and Temporal Exploration Software:
  - Spreadsheets (e.g., Microsoft Excel, Lotus 1-2-3, Quattro Pro)
  - Statistical packages (e.g., S-PLUS, SYSTAT, Statsoft, SAS)
  - Other similar statistical and GIS-based software

Summary

- Isoprene is typically the most abundant biogenic VOC and is a PAMS target hydrocarbon.
- Biogenic hydrocarbons may play an important role in ozone formation.

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